Catalytic hydrogenation of acrylonitrile–butadiene copolymers by a series of osmium complexes

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Abstract

The activity of a series of osmium complexes as catalysts for the hydrogenation of nitrile-butadiene copolymers (NBR) was studied under 3.42 MPa hydrogen pressures and at 130°C in monochlorobenzene. On the basis of the correlation of phosphine ligand properties with the catalytic activities of complexes, the complexes studied are divided into three classes: class I (bulky monophosphines with Tolman's cone angle $\geq 160°$) $OsHCl(CO)(O_2)(PR_3)_2$ ($PR_3 = P^iPr_3$, PCy_3, PCy_2Ph); class II (small monophosphines) $OsHCl(CO)(PR_3)_3$ ($PR_3 = PPh_3$, $P(m\text{-}C_6H_4Me)_3$); class III (diphosphines) $OsHCl(CO)(PPh_3)(dppp)$ ($dppp = Ph_2P(CH_2)_3PPh_2$). In general, the activity of these complexes decreases as follows: class I > class II > class III. This trend is mainly attributed to the ease of dissociation of a ligand from an 18-electron complex to generate a 16-electron species ($O_2 > PR_3 > dppp$) in the catalytic process. In the case of complexes of class I as catalysts, their activities increase in the order: $PCy_2Ph \ll P^iPr_3 < PCy_3$. While this activity trend does not appear to correlate with the steric effect based on Tolman's cone angles, it is in good agreement with the electronic effect, which is evaluated based on the infrared v_{CO} values of these complexes. The catalytic activity of these complexes increases with the decrease of v_{CO} value, which is consistent with the increase of the donor power of phosphine ligands. This indicates that the activity of these complexes are predominately dependent on the electronic properties of phosphines and, in conjunction with the kinetic isotope effect, the rate determining step of the catalytic process would be an H_2 bond breaking related process or an olefin insertion into an Os–H bond. With complexes of classes II and III, a complex containing a bulky, strong σ-donor and weak π-acceptor phosphine is a good catalyst whereas that containing a chelating phosphine ligand would be a poor catalyst. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; Nitrile-butadiene rubber; Phosphines; Osmium complexes

1. Introduction

Homogeneous catalytic hydrogenation of diene-based polymers and copolymers has been extensively studied during the past two decades [1,2]. Interest in the catalytic modification of polymers has arisen as a result of its recognized importance as a practical approach to the production of specialty materials. In particular, the hydrogenation of nitrile-butadiene copolymers (NBR) provides the

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hydrogenated nitrile-butadiene copolymers (HNBR) that cannot be generated by conventional poly-merization approaches (Scheme 1). The selective reduction of the olefinic group present in NBR improves its physical, mechanical and chemical properties, as such, the resulting product (HNBR) can be used as a robust elastomer under severe conditions [3].

A variety of transition metal complexes, generally containing group VIII transition metals of the second row, are known as catalysts for the homogeneous hydrogenation of NBR [1,2,4]. Representative examples include complexes such as $Rh(PPh_3)_3Cl$, $RuCl_2(PPh_3)_3$, and Pd(carboxylates). In contrast, the catalytic application of the complexes that contain a group VIII transition metal of the third row in the hydrogenation of NBR has not been reported until a recent discovery from this laboratory [5,6]. This is consistent with the scenario that complexes containing 4d metals are widely used as catalysts for simple olefin hydrogenation [7–10]. It is generally accepted that the strong bonding between 5d metal and ligand could prohibit ligand dissociation, which is an essential step involved in a catalytic hydrogenation process. Thus complexes of this type are often found to be less active or inactive catalysts. Recent studies mainly by Esteruelas et al. [11–14] have demonstrated that osmium complexes such as $OsHCl(CO)(P^iPr_3)_2$ are active catalysts for olefin hydrogenation. We have reported that, in the case of selective hydrogenation of NBR, $OsHCl(CO)(L)(PCy_3)_2$ (L = vacant or O_2) is a much more active catalyst than complexes $Rh(PPh_3)_3Cl$ and $RuHCl(CO)(L)(PCy_3)_2$ (L = vacant or O_2) at industrial conditions ($P > 2$ MPa, $T > 100°C$) [5,6,15,16]. Interestingly, kinetic studies suggest that the hydrogenation reactions catalyzed by complexes of this type proceed by
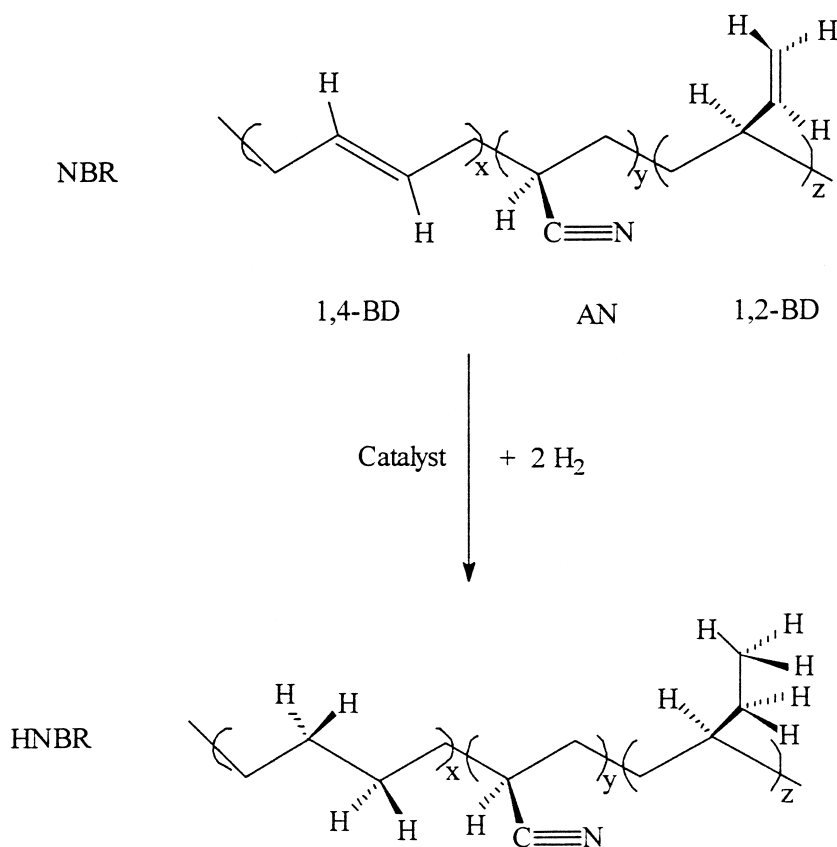
Scheme 1. Structures of NBR and hydrogenated NBR (HNBR).

different mechanisms, which are not fully understood [6,11]. Although there is an increasing number of reports on the catalytic application of osmium complexes, the complexes employed are still limited. To the best of our knowledge, there are no reports in the literature on the systematical examination of the catalytic activity of osmium complexes for both small olefin hydrogenation and large olefin hydrogenation such as NBR hydrogenation. It is well known that the catalytic activity and selectivity of metal phosphine complexes can be changed significantly by changing phosphine ligands [7,17–19]. Thus it was hoped that, by tuning the electronic and steric properties of phosphines [20], a better understanding of the reactivity features of osmium complexes of this type might be gained.

In this paper we wish to report the synthesis and characterization of a number of osmium complexes containing phosphines. These complexes, together with those of known osmium complexes used for this study, include: $OsHCl(CO)(L)(PR_3)_2$ (L = vacant, O_2; $PR_3 = P^iPr_3$, PCy_3, PCy_2Ph); $OsHCl(CO)(PR_3)_3$ ($PR_3 = PPh_3$, $P(m-C_6H_4Me)_3$); $OsHCl(CO)(PPh_3)(dppp)$. Both the activity of these complexes and a related comparison, for catalytic hydrogenation of NBR, are also presented.

2. Experimental

2.1. General

All manipulations for the synthesis of organometallic complexes were carried out under a N_2 atmosphere in a Vacuum Atmospheres drybox or under a N_2 atmosphere using conventional Schlenk techniques. IR spectra were obtained on a Nicolet 520 FT-IR spectrometer over the range 400–4000 cm^{-1}. The ^1H NMR, $^{31}P\{^1H\}$ NMR and $^{13}C\{^1H\}$ NMR spectra were recorded on a Bruker 200, Bruker 250, or a Bruker 300 MHz spectrometer.

2.2. Materials and reagents

Osmium trichloride hydrate was purchased from Strem Chemical. Complexes $OsHCl(CO)-(O_2)(PCy_3)_2$ [21] and $OsHCl(CO)(PPh_3)_3$ [22] were prepared according to the published literature procedures. The nitrile-butadiene rubber (Krynac 38.50) was supplied from Bayer, which contained 62 wt.% butadiene (80% *trans*, 15% *cis*, 5% vinyl isomerization) with an M_n of 70 000. This material was used without further purification.

All reagent grade solvents were used as received and were thoroughly degassed before use. The ligands, triphenylphosphine, dicyclohexylphenylphosphine, tricyclohexylphosphine, tritolylphosphine and bis(diphenylphosphino)propane were purchased from Strem Chemical and used without purification. Oxygen-free hydrogen gas (99.99%) was obtained from Linde-Union Carbide Canada.

2.3. Synthesis of $OsHCl(CO)(PCy_2Ph)_2$

To a mixture of osmium trichloride hydride (0.315 g, 1.06 mmol) and dicyclohexylphenylphosphine (1.54 g, 5.61 mmol) was added 10 ml methoxyethanol. The reaction mixture was stirred vigorously, heated to reflux and kept refluxing for 48 h, during which time a reddish brown precipitate was formed. After it was cooled to ambient temperature, the supernatant was removed via a syringe. The residue was washed with methanol and hexane to give 0.488 g (57%) of an orange solid. IR (CH_2Cl_2, cm^{-1}): 1963 (w, Os–H), 1903 (s, CO); ^1H NMR (CD_2Cl_2): −33.2 (t, $^2J_{PH}$ = 12.5 Hz); $^{31}P^1H$ NMR (CD_2Cl_2): 39.4 (s); $^{13}C^1H$ NMR (CD_2Cl_2): 179.1 (br s, CO).

2.4. Synthesis of OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$

An orange suspension of OsHCl(CO)(PCy$_2$Ph)$_2$ (51.42 mg, 0.0640 mmol) in 5 ml hexane was stirred under a stream of oxygen at room temperature for 14 min during which time a white precipitate formed. The supernatant was removed and the precipitate was washed with hexane to give the product as white solids 45.15 mg (84%). IR (CH$_2$Cl$_2$, cm^{-1}): 1965 (s, CO), 1915 (w, Os–H), 896 (O$_2$); ^{1}H NMR (CD$_2$Cl$_2$): − 1.80 (t, $^2J_{PH} = 31.2$ Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 11.3 (s).

2.5. Synthesis of OsHCl(CO)(P(m-C$_6$H$_4$CH$_3$)$_3$)$_3$

A mixture of OsCl$_3 \cdot x$H$_2$O (154.10 mg, 0.520 mmol) and P(m-C$_6$H$_4$CH$_3$)$_3$ (790.79 mg, 2.60 mmol) in 5 ml methoxyethanol was refluxed for 42 h, during which time a white precipitate formed. After it was cooled to room temperature, the supernatant was removed and the residue was washed with methanol and hexane to give the product as a white powder (412.74 mg, 68%). IR (CH$_2$Cl$_2$, cm^{-1}): 2057 (W, Os–H), 1909 (s, CO); ^{1}H NMR (CD$_2$Cl$_2$): 2.05 (s, 18H), 1.96 (s, 9H), −7.11 (dt, $^2J_{PH} = 86.6$ Hz, $^2J_{PH} = 25.0$ Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 6.89 (d, $^2J_{PP} = 11.4$ Hz, 2P), −10.4 (t, $^2J_{PP} = 11.4$ Hz, 1P); ^{13}C^{1}H NMR (CD$_2$Cl$_2$): 182.9 (dt, $^2J_{CP} = 8.75$ Hz, $^2J_{CP} = 6.19$ Hz, CO), 21.6 (s, CH$_3$), 21.5 (s, 2CH$_3$).

2.6. Synthesis of OsHCl(CO)(PPh$_3$)(dppp)

A mixture of OsHCl(CO)(PPh$_3$)$_3$ (203.63 mg, mmol) and bis(diphenylphosphenyl)propane in 4 ml p-xylene was refluxed for 30 min. After it was cooled to room temperature, hexane (10 ml) was added whereupon a white precipitate formed. The supernatant was removed and the residue was washed with ethanol to give the product as a white solid 114 mg (63%). IR (CH$_2$Cl$_2$, cm^{-1}): 2026 (W, Os–H), 1909 (s, CO); ^{1}H NMR (CD$_2$Cl$_2$): −6.6 (ddd, $^2J_{PH} = 84$ Hz, $^2J_{PH} = 23$ Hz, $^2J_{PH} = 18$ Hz); ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$): 14.6 (dd, $^2J_{PP} = 258$ Hz, $^2J_{PP} = 18$ Hz), −7.9 (dd, $^2J_{PP} = 258$ Hz, $^2J_{PP} = 16$ Hz), −21.1 (dd, $^2J_{PP} = 18$ Hz, $^2J_{PP} = 16$ Hz); ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$): 183.5 (m, CO).

2.7. Hydrogenation reactions

The hydrogenation experiments were carried out in a autoclave reactor of total volume of 300 ml. The procedures for these experiments are similar to those described previously [4]. The monochlorobenze (75 ml) solution of NBR (1.55 g) was degassed by charging the reactor with hydrogen to about 3.42 MPa, stirred vigorously under hydrogen for a couple of minutes, and then venting. This cycle was repeated for three times, followed by bubbling hydrogen through the solution to ensure that any oxygen in the system was thoroughly removed. The system was heated to 130°C and maintained at this temperature for 1 h to reach the system equilibrium. The monochlorobenze (25 ml) solution of catalyst (0.01 mmol) was then transferred into the reactor. The reaction was kept at 130°C and the pressure of the system was maintained at 3.42 MPa during the catalytic process. The reaction was monitored by periodically analyzing the IR spectra of reaction samples. The degree of hydrogenation was calculated according to the published method [23].

2.8. Measurement of reaction rates

A gas uptake apparatus, which consists of a batch reactor, a hydrogen gas supply unit, a temperature control unit and a computer control system, was used for kinetic measurements [24]. The experimental procedures are similar to those described previously for Ru(CH = CH-

(Ph))Cl(CO)(PCy$_3$)$_2$ catalyst [16]. A known amount of polymer (Krynac 38.50) was dissolved in 150 ml monochlorobenzene. The solution was then thoroughly degassed and heated to a desired temperature. After it was kept at this temperature for 45 min, a catalyst was added to start the reaction. The reaction temperature and pressure in the reactor were maintained constant throughout hydrogenation. The hydrogen gas consumption was continuously analyzed by a computer system. The final percentage of NBR hydrogenation was calibrated by using the value obtained from the IR spectrum of the hydrogenated polymer.

3. Results and discussion

3.1. Synthesis and characterization

3.1.1. The complexes OsHCl(CO)(L)(PR$_3$)$_2$ (1: L = vacant, PR$_3$ = PCy$_2$Ph; 2: L = O$_2$, PR$_3$ = PCy$_2$Ph; 3: L = PR$_3$ = P(m-C$_6$H$_4$CH$_3$)$_3$)

Complex **1** and **3** were readily prepared by refluxing OsCl$_3$ · xH$_2$O with an excess of either PCy$_2$Ph or P(m-C$_6$H$_4$CH$_3$)$_3$ in methoxyethanol in a similar way to the reported methods for the synthesis of analogous complexes [25,26]. Compound **1** reacts with oxygen in hexane to give compound **2** in good yield. The spectroscopic parameters of compounds **1**, **2**, and **3** are similar to those of OsHCl(CO)(P^{i}Pr$_3$)$_2$ [26], OsHCl(O$_2$)(CO)(P^{t}Bu$_2$Me)$_2$ [13], and OsHCl(CO)(PPh$_3$)$_3$ [27]. Accordingly, they are assigned to analogous structures.

3.1.2. The complex OsHCl(CO)(PPh$_3$)(dppp), 4

When OsHCl(CO)(PPh$_3$)$_3$ was treated with dppp in refluxing p-xylene, the new compound **4** was obtained. Compound **4** was characterized by IR, ^{1}H, ^{31}P{^{1}H}, and ^{13}C{^{1}H} NMR spectroscopy. The ^{31}P{^{1}H} spectrum showed three resonances at δ 14.6 ($^2J_{PP}$ = 258 Hz, $^2J_{PP}$ = 18 Hz), -7.9 ($^2J_{PP}$ = 258 Hz, $^2J_{PP}$ = 16 Hz), and -21.1 ($^2J_{PP}$ = 18 Hz, $^2J_{PP}$ = 16 Hz), indicating three distinct phosphines. The strong coupling (258 Hz) between the two phosphines indicates their *trans* arrangement while the weak couplings (18 Hz, 16 Hz) suggests that they are oriented *cis* to each other. In the ^{1}H spectrum, a high field signal at δ -6.6 ($^2J_{PH}$ = 84 Hz, $^2J_{PH}$ = 23 Hz, $^2J_{PH}$ = 18 Hz) was attributed to the hydride where its appearance as a doublet of doublets of doublets is due to the couplings between the hydride and the three coordinated phosphines. The large coupling constant (84 Hz) indicates that the hydride is oriented *trans* to one phosphine whereas the other small coupling constants (23 Hz, 18 Hz) suggests that the hydride is *cis* to the other two phosphines. The ^{13}C{^{1}H} NMR spectrum contained a resonance at δ 183.5 in the range of typical osmium terminal carbonyl [28]. Thus the spectroscopic data clearly establish that compound **4** has the structure as shown in Eq. (2).

3.1.3. The Reactions of OsCl$_3$ · xH$_2$O with P(O^{t}Bu)$_3$ or P^{t}Bu$_3$

In order to expand the scope of complexes studied, attempted preparations of OsHCl(CO)L$_2$ (L = P(O^{t}Bu)$_3$, P^{t}Bu$_3$) by the reactions of OsCl$_3$ · xH$_2$O with five equivalents of either P(O^{t}Bu)$_3$ or P^{t}Bu$_3$ in refluxing methoxyethanol were not successful. While the reason for the former one might be the thermal stability of P(O^{t}Bu)$_3$, the latter one is most likely due to the steric hindrance [29].

3.2. Catalytic hydrogenation

The hydrogenation reactions of NBR, catalyzed by a series of osmium complexes and Wilkinson's catalyst, were carried out under a hydrogen pressure of 3.42 MPa at 130°C in monochlorobenzene solutions. The activities of these complexes are listed in Table 1. The IR spectra of the hydrogenated

Table 1
The hydrogenation of NBR[a]

Catalyst	Hydrogenation (%)	Reaction time (h)	Turnover rate[b] (mol (mol Metal)$^{-1}$ h^{-1})
OsHCl(CO)(O$_2$)(PCy$_3$)$_2$	99.7	0.5	3546
OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$	63.3	0.5	2251
OsHCl(CO)(P(m-C$_6$H$_4$Me)$_3$)$_3$	23.1	1	413
OsHCl(CO)(PPh$_3$)$_3$	12.5	1	222
OsHCl(CO)(PPh$_3$)(dppp)	10.3	18	10
Rh(PPh$_3$)$_3$Cl	91.7	0.5	3261

[a] Reaction conditions: Catalyst $= 1 \times 10^{-5}$ mol, olefin in NBR (Krynac 38.50) $= 1.78 \times 10^{-2}$ mol, solvent $= 100$ ml monochlorobenzene, temperature $= 130°C$, $P_{H_2} = 3.42$ MPa.
[b] Turnover rates were calculated based on the averaged number of moles of olefin reduced per mol of metal during a period of time specified.

NBR samples demonstrated that these catalysts selectively reduce the olefinic double bonds present in NBR with the nitrile group remained intact.

The osmium complexes studied can be divided into three classes. Class I includes O$_2$ adducts that contain steric bulky phosphines, namely, OsHCl(CO)(O$_2$)(PCy$_3$)$_2$, OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$. The reasons that these complexes were chosen instead of their five-coordinate precursors are: (a) these complexes are much more stable than their precursors such as OsHCl(CO)(PCy$_3$)$_2$, OsHCl(CO)(PCy$_2$Ph)$_2$, as such, they are easy to handle and give reproducible results; (b) their activities should follow the similar trend to those of the precursors as they lose oxygen upon heating to generate the corresponding five-coordinated complexes (Eq. (1)) [30]. Class II includes those complexes that contain relatively small monophosphines, such as, OsHCl(CO)(PPh$_3$)$_3$ and OsHCl(CO)(P(m-C$_6$H$_4$CH$_3$)$_3$)$_3$. Class III are those compounds that contain chelating phosphines, namely, OsHCl(CO)(PPh$_3$)(dppp). In order to compare the activities of these complexes with a well known catalyst, the hydrogenation reaction by Wilkinson's catalyst, Rh(PPh$_3$)$_3$Cl, was also carried out under the same conditions.

The catalytic activity of these complexes was found to be in the order: OsHCl(CO)(O$_2$)(PCy$_3$)$_2$ > Rh(PPh$_3$)$_3$Cl > OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$ > OsHCl(CO)(P(m-C$_6$H$_4$Me)$_3$)$_3$ > OsHCl(CO)(PPh$_3$)$_3$ > OsHCl(CO)(PPh$_3$)(dppp). Thus their activities appear to follow a general trend: class I > class II > class III. This clearly demonstrates the effect of phosphine ligands on the catalytic activities of these complexes.

There are precedents that show the effect of phosphine ligands on hydrogenation mechanism [6,11]. It is generally accepted that all these reactions proceed by initial generation of a five-coordinate species (Eq. (1)) [11,14,31,32].

$$(1)$$

L = PCy$_3$, PCy$_2$Ph
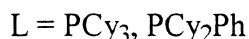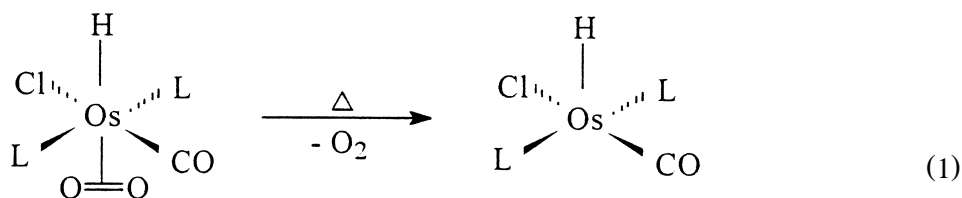
Several important features require some comments. First, as the reactions were carried out under high hydrogen pressure, the oxygen dissociates completely from its six-coordinate adducts to give the corresponding five-coordinate species. Thus, in the case of complexes of type I, the effect of oxygen on the rate of the reactions is negligible. Second, the phosphine ligand opposite to the hydride is most likely to dissociate since the trans effect of the strong σ-bonding hydride labilizes the phosphine ligand *trans* to it. Third, a dissociated phosphine ligand, especially in the case of a chelating ligand such as dppp, will compete effectively with olefins for vacant coordination sites thereby reducing the rate of the reaction (Eqs. (2) and (3)). Therefore, the hydrogenation reactions catalyzed by class I complexes are expected to be faster than those catalyzed by both class II and class III where complexes of class III are the poorest catalysts.

$$\text{(2)}$$

$$\text{(3)}$$

$$PR_3 = PPh_3, P(m\text{-}C_6H_4CH_3)_3$$
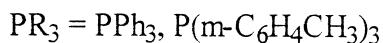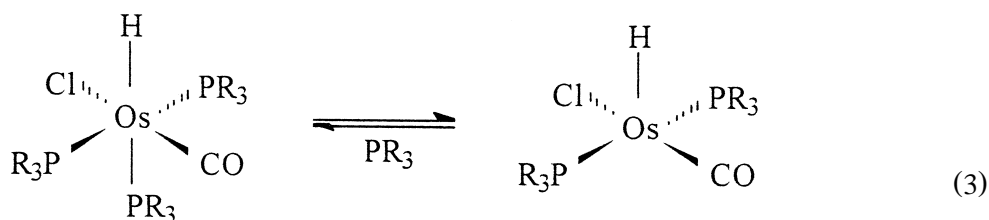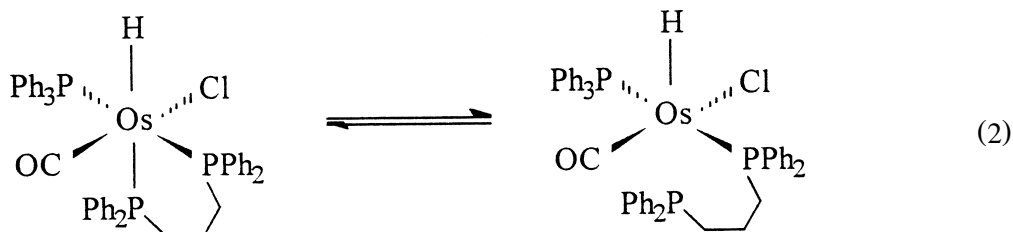
3.2.1. Comments on the activities of class I complexes

In an attempt to accurately compare the activity of these complexes for NBR hydrogenation, a number of kinetic experiments were carried out under the same conditions. The hydrogenation profiles are composed of two parts. One is the initial rapid hydrogenation, which is attributed to the hydrogenation of both a 15% *cis*-olefin and a 5% vinyl isomer present in NBR, the other is the hydrogenation of trans isomer (80%), which follows a first-order regression model. This is in accord with those observed in a detailed kinetic study on NBR hydrogenation with $OsHCl(CO)(O_2)(PCy_3)_2$ [31]. The rate constants given in Table 4 are obtained from the regression of the second part of hydrogenation profile.

As shown in Tables 1 and 4, the catalytic activity of $OsHCl(CO)(O_2)L_2$ ($L = PCy_3$, PCy_2Ph, P^iPr_3) decreases in the order: $PCy_3 > P^iPr_3 > PCy_2Ph$. This is in line with the donor power of the phosphines as a better donor ligand such as PCy_3 makes osmium more electron-rich thereby enhancing the $d\pi-p\pi^*$ back bonding between osmium and carbonyl, thus reducing the carbonyl stretch frequency (Table 2).

Table 2
Electronic parameters ν for catalysts

Catalyst	ν_{CO} (CH$_2$Cl$_2$, cm^{-1})
OsHCl(CO)(O$_2$)(PCy$_3$)$_2$	1950
OsHCl(CO)(PCy$_3$)$_2$	1886
OsHCl(CO)(O$_2$)(P^{i}Pr$_3$)$_2$	1953
OsHCl(CO)(P^{i}Pr$_3$)$_2$	1887
OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$	1965
OsHCl(CO)(PCy$_2$Ph)$_2$	1963
OsHCl(CO)(P(m-C$_6$H$_4$Me)$_3$)$_3$	1908
OsHCl(CO)(PPh$_3$)$_3$	1913
OsHCl(CO)(PPh$_3$)(dppp)	1909

The steric effect is typically examined by means of Tolman's cone angle, which is a measure of a phosphine size [20]. Table 3 shows that phosphine bulkiness increases in the order: P^{i}Pr$_3$ < PCy$_2$Ph < PCy$_3$. This trend is not in agreement with the activity order observed for the corresponding phosphine complexes (Table 4). Although the size of P^{i}Pr$_3$ (160°) is similar to that of PCy$_2$Ph (162°), their activities are very different. Complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ is 11 times as active as OsHCl(CO)(PCy$_2$Ph)$_2$. In contrast, although the PCy$_3$ (170°) is much bulkier than P^{i}Pr$_3$ (160°), their difference in activity is much smaller. This indicates that the steric effect does not play a major role in governing the activity of these complexes.

A kinetic study by Parent et al. [31] shows that, in the case of NBR hydrogenation in the presence of OsHCl(CO)(O$_2$)(PCy$_3$)$_2$, a kinetic isotope effect in terms of k_{H2}/k_{D2} value of 1.65 ± 0.51 is observed indicating that the rate determining step of the catalytic process could be the oxidative addition of H$_2$, which is also involved in the H/η^2-H$_2$ rearrangement process [11] or the olefin insertion into an Os-H bond, or the reductive elimination to form the corresponding saturated products. Although it is not obvious what effects a phosphine ligand will have electronically on the rate of an olefin insertion into an Os–H bond, an increase of electron density on osmium by increasing electron donor power of phosphine ligands will generally facilitate the oxidative addition of H$_2$ and, on the other hand, retard reductive elimination of the hydrogenated products [33,34]. In conjunction with the experimental results described earlier where a complex OsHCl(CO)(O$_2$)L$_2$ (L = PCy$_3$, PCy$_2$Ph, P^{i}Pr$_3$) with an electron richer phosphine is a better catalyst, this suggests that the rate determining step might be either oxidative addition of H$_2$ and the related H/η^2-H$_2$ rearrangement to generate cis geometry or olefin insertion.

It is well documented that the hydride-olefin insertion requires that the alkene carbons and the M–H bond in a nearly coplanar arrangement, indicating such cis(olefin, M–H) geometry must be

Table 3
Cone angles for phosphine ligands[a]

Phosphine	θ (°C)
P^{i}Pr$_3$	160
PCy$_3$	170
PCy$_2$Ph	162
P(m-C$_6$H$_4$Me)$_3$	148[b]
PPh$_3$	145

[a] Ref. [39].
[b] Ref. [40].

Table 4
Summary of kinetic data[a]

Catalyst	$k \times 10^3$, s^{-1}
OsHCl(CO)(O$_2$)(PCy$_2$Ph)$_2$	0.128
OsHCl(CO)(O$_2$)(PCy$_3$)$_2$	3.57[b]
OsHCl(CO)(O$_2$)(P^{i}Pr$_3$)$_2$	1.41[b]
OsHCl(CO)(P(m-C$_6$H$_4$Me)$_3$)$_3$	0.0106

[a] Reaction conditions: catalyst concentration = 80 μM, olefin (Krynac 38.50) concentration = 275 mM, temperature = 130°C, hydrogen pressure = 2.4 MPa, solvent = 150 ml monochlorobenzene.
[b] Refs. [6,31].

satisfied [33]. In the case of complexes OsHCl(CO)L$_2$ (L = PCy$_3$, PCy$_2$Ph, P^{i}Pr$_3$), the direct coordination of olefin will lead to the formation a trans(olefin, hydride) species, an unrealistic disposition for olefin insertion. Esteruelas et al. [11] found that OsHCl(CO)(P^{i}Pr$_3$)$_2$ reacts with H$_2$ to give OsHCl(η^2–H$_2$)(CO)(P^{i}Pr$_3$)$_2$ where the hydride can undergo exchange with dihydrogen ligand. Thus complex OsHCl(CO)(P^{i}Pr$_3$)$_2$ becomes an active catalyst under hydrogen by such a crucial H/η^2-H$_2$ exchange process to isomerize *trans*(hydride, dihydrogen)-OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$ to *cis*(hydride, dihydrogen)-OsHCl(η^2-H$_2$)(CO)(P^{i}Pr$_3$)$_2$, followed by dissociation of a dihydrogen ligand and an olefin coordination *cis* to the hydride. Additional results from NMR and theoretical studies [35] confirm that, in the case of relatively small values of kinetic isotopic effect, the H/η^2-H$_2$ exchange most likely proceeds through a series of trihydride intermediates.

The influence of phosphine on the rate of an olefin insertion into an Os−H bond is complex. In general, the stronger the bonding of a coordinated olefin is, the slower the olefin insertion will be [33]. Since the bonding between a metal and an olefin depends on the electronic properties of both phosphine and olefin, the rate of olefin insertion is not correlated well with the elelctronic property of phosphine. Nevertheless, a detailed kinetic study of NBR hydrogenation by OsHCl(O$_2$)(CO)(PCy$_3$)$_2$ demonstrates that the olefin insertion is a plausible rate determining step [31].

3.2.2. Comments on the activities of classes II and III complexes

As described earlier, the first common step of catalytic processes in the presence of these complexes as catalysts is a phosphine ligand dissociation (Eqs. (2) and (3)). Thus the easier a phosphine dissociation is, the more active a complex would be. As complex OsHCl(CO)(PPh$_3$)(dppp) contains a chelating ligand, it is the most stable species among the complexes studied. On the other hand, it is the poorest catalyst.

The activity difference between OsHCl(CO)(P(m-C$_6$H$_4$Me)$_3$)$_3$ and OsHCl(CO)(PPh$_3$)$_3$ (Table 2) can be rationalized in terms of phosphine effects. The catalytic processes may be considered as two parts: (a) a phosphine dissociation (Eq. (3)); (b) a catalytic cycle similar to those described for complexes of class I. It is well documented that, in the case of an 18-electron octahedral complex, the rate of ligand dissociation increases with the increase of steric bulkiness whereas the electronic factors of ligands may not be correlated well with the rate of ligand dissociation [36–38]. With this in mind, the steric bulky P(m-C$_6$H$_4$Me)$_3$ (Table 3) is expected to accelerate its dissociation. In addition, the P(m-C$_6$H$_4$Me)$_3$ is a better σ-donor and weaker π-acceptor than PPh$_3$ as evidenced in the carbonyl frequencies in their corresponding complexes (Table 2). Thus the Os−P(m-C$_6$H$_4$Me)$_3$ bonding would be weakened as a result of the buildup of electron density along the H−Os−P(m-C$_6$H$_4$Me)$_3$ axis. Furthermore, a stronger σ-donor ligand (P(m-C$_6$H$_4$Me)$_3$) would stabilize the electron deficient transition state. Therefore, both the electronic effects and steric effects favor P(m-C$_6$H$_4$Me)$_3$

dissociation. As described for complexes of class I where a better σ-donor phosphine would generate a better catalyst, by the same token, after phosphine dissociation, species $OsHCl(CO)(P(m\text{-}C_6H_4Me)_3)_2$ is expected to be a better catalyst than $OsHCl(CO)(PPh_3)_2$. In short, on the basis of both phosphine dissociation and the activity of the generated species, $OsHCl(CO)(P(m\text{-}C_6H_4Me)_3)_3$ would be a better catalyst.

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